Plasma-catalysis destruction of aromatics for environmental clean-up: Effect of temperature and configuration

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Abstract

A non-thermal, atmospheric pressure, packed-bed plasma reactor has been used to study the effect of temperature on the plasma-catalytic destruction of toluene and benzene in air using two catalyst positions. TiO_2 and γ-Al_2O_3 supports, and Ag (0.5 wt.%) impregnated catalysts of both supports, were used to determine their effects. The reactor (in the one-stage configuration) or the downstream catalyst (in the two-stage arrangement) could be heated to ~600 °C and the destruction efficiencies for toluene and benzene were determined. Plasma catalysis is more effective at destroying benzene and toluene than both conventional thermal-catalysis and plasma alone. Toluene is destroyed much more efficiently than benzene, regardless of the temperature of the system and the reactor configuration. A one-stage, plasma-catalysis configuration is found to be more effective at destroying both toluene and benzene than a two-stage configuration. Plasma catalysis offers no advantage over thermal catalysis for destroying both pollutants in the two-stage configuration.
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1. Introduction

Benzene and toluene are common solvents used in the chemical and pharmaceutical industries and their release into the atmosphere is regulated. They are also used as additives to gasoline fuels and are commonly associated with vehicle emissions and fuel handling. Both benzene and toluene pose a danger to human health. These aromatic pollutants are also of particular interest as they have been shown to be present in modern, unventilated homes as indoor airborne pollutants with levels which are 2–10 times higher than those found outdoors [1]. Likely indoor sources of benzene and toluene include paint, tobacco smoke, synthetic furniture, cleaning products and insulating products [2]. The aromatic structure of these compounds makes their route of decomposition different to other pollutants. Specifically, benzene has a low reactivity (much lower than that of other aromatics such as toluene and xylene) making it much harder to decompose, especially using

radical-related chemical methods [3]. It has been shown that non-thermal plasma technology has considerable potential for the destruction of pollutants in waste gas streams and in indoor air [4,5].

This present study of the destruction of benzene and toluene is part of ongoing work in our laboratory looking at the mechanism of plasma-activated catalysis by studying the effect of temperature on the process [6–8]. We have previously shown that plasma-activated catalysis is a more successful method for the destruction of benzene and toluene than conventional thermal catalysis over a temperature range up to 500 °C [6]. It has been suggested that two different mechanisms for destruction may be taking place at low and high temperatures for the plasma-catalysis process; at lower temperature, the plasma-activation consists mainly of gas-phase destruction but at higher temperatures the plasma causes direct activation of the catalyst giving enhanced destruction [6]. Overall, better destruction of toluene is seen than of benzene, regardless of the catalyst [6]. This work was extended to look at the kinetics of the plasma-catalytic decomposition of toluene on γ-alumina support, MnO_2–alumina and Ag–alumina catalysts [8]. A comparison between the one-stage, with the catalyst inside the

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reactor, and two-stage, with the catalyst downstream of the reactor, configurations was made over a large temperature range. The mechanism of plasma activation was deduced through the use of an Arrhenius plot. It was found that there is not a big difference between the activation energy for thermal catalysis and the two-stage plasma-catalyst systems but that plasma could activate a catalyst placed inside the discharge in the one-stage arrangement, reducing the activation energy in the case of Ag–alumina or increasing the number of active surface sites when using MnO_2–AlO_2 [8].

We have also looked at the effect of temperature on the plasma-catalytic destruction of dichloromethane (DCM) and again find that plasma catalysis is more successful at destroying the pollutant than plasma or catalysis-alone over the range of 125–400 °C [7]. We can achieve comparable reduction in the pollutant concentration to conventional thermal catalysis but at a greatly reduced operating temperature. This gives an energy saving of ~33% for plasma-activated catalysis compared with conventional thermal activation and reduces possible problems of catalyst degradation by processes such as poisoning, coking and sintering and may allow the use of less thermally stable catalysts. This is a beneficial synergistic effect which allows higher destructions at lower temperatures by the plasma-activation of the catalyst giving reduced energy consumption which may be due to electron-induced processes, UV photons, short-lived radicals and surface discharges formed in the discharge and is likely to be specific to the catalyst used [7].

Demidiouk and Chae [9] found that plasma treatment significantly increases the efficiency of the catalytic decomposition of toluene in a two-stage configuration. The catalyst was heated from 150 to 240 °C whilst the plasma reactor was kept at room temperature. When the catalyst alone was heated the destruction increased from 10 to 85%; for the plasma-catalysis destruction increased from 60 to 95% over a similar temperature range [9]. Demidiouk et al. [10]. studied the removal of toluene in air using a plasma-catalytic system with a Pt/Al_2O_3 catalyst. They found that the addition of a catalyst in a two-stage configuration increased the removal [10].

This work investigates the effect of temperature on the plasma-catalytic destruction of benzene and toluene but also studies the effect of the position of the catalyst. It also looks at the performance of different supports and metal impregnated catalysts and their effect on the plasma destruction of benzene and toluene. The reactor (in the one-stage configuration) or the downstream catalyst (in the two-stage arrangement) could be heated to ~600 °C and the destruction efficiencies for toluene and benzene were determined for plasma alone, catalyst alone and the combined plasma-catalyst configuration.

2. Experimental

2.1. Experimental background

This work has been carried out using a similar experimental setup to previous work [7,8] which is slightly different to that used for a previous collaborative study of the same aromatics [6]. The arrangement used in these experiments is an automated, computer-controlled version used in a previous study of adaptive control of NO removal in a plasma system [11]. The main control system included a gas blending system, the plasma reactor, its power supply and heater, a FTIR spectrometer and a control computer.

The gas flow through the plasma reactor was measured and maintained by a series of mass flow controllers (MKS 1179A 10–10,000 sccm) operating from a control unit (MKS 647B) which was set and interrogated by the computer. The pressure of the reactor was maintained at 1 bar monitored by a capacitance manometer (MKS Baratron, 0–5000 mbar.) The concentrations in the exit steam were detected and analysed by an on-line fast FTIR infrared spectrometer (GASMET DX-4010, 8 cm^{-1} resolution, high path gas cell of length 9.8 m). The measured values were transferred to the control computer running the FTIR software and the system was run through an automated LabVIEW control program [11].

The carrier gas used in these experiments was synthetic air, made by blending nitrogen (800 sccm) and oxygen (200 sccm), (BOC gases, used as supplied) to give a total gas flow of 1 l min^{-1}. The flow of benzene, C_6H_6, (BDH, 99% purity, used as supplied) or toluene, C_7H_8, (Hopkins and Williams, 99% purity, used as supplied) was varied to achieve a concentration of 500 ppm. The gases passed through a plasma reactor packed with $BaTiO_3$ beads (3.5 mm diameter). The reactor consisted of a quartz tube of 25 mm internal diameter with two electrodes ~170 mm apart, as discussed and shown previously [7]. An ac voltage of 16 kV$_{pk-pk}$ at a frequency of 9.6 kHz was applied between the electrodes. The heating arrangement for the system has also been described before [7]. In a one-stage configuration, the plasma discharge operates in the same region as the catalyst and the gaps between the $BaTiO_3$ beads were filled with the catalyst. A ratio of 5:12 of catalyst to $BaTiO_3$ beads is used, as this has been found previously to work well [12]; this means for 17 ml of $BaTiO_3$ beads, 7 ml of catalyst is used. In the two-stage configuration, 1.7 ml of the catalyst was placed ~10 cm downstream from the reactor in its own quartz tube [8]. A direct comparison was also made between the one- and two-stage systems to determine if the amount of catalyst used affected the results; this was done by modifying the two-stage system to use 7 ml catalyst for the destruction of toluene.

The electrical power supplied to the discharge was controlled by varying the applied voltage using digitised control under LabVIEW [11]. The voltage and current supplied to the plasma reactor are monitored in real time by two digital sampling modules (Pico ADC-200, 10 MHz bandwidth, 8-bit, 20 MS s^{-1}) using a calibrated high voltage probe and measuring the current across a 1 kΩ resistor in the return earth path from the reactor. This gives an average power of ~1 W for a voltage of 16 kV, giving an overall deposited energy density of 60 J L^{-1}, determined as described previously [7].

2.2. Catalyst preparation

The support materials TiO_2 (Alta Aesar) and γ-Al_2O_3 (Geejay Chemicals Ltd.), were used as supplied and ground down to 500–850 μm in size. Impregnated catalysts, with

Table 1
BET results for the surface areas of the parent catalysts and supports

Catalyst	Surface area ($m^2 g^{-1}$)
TiO_2	137.38
Al_2O_3	276.08
Ag/TiO_2	28.449
Ag/Al_2O_3	191.26

different amounts of metal on the surface were prepared, as detailed below. The silver (Ag) 0.5 wt.% on γ-Al_2O_3 catalyst was prepared by loading the silver on the γ-Al_2O_3 chips by an impregnation method using $AgNO_3$. The $AgNO_3$ was heated in an oven to ∼600 °C for 1 h to remove any water and then dissolved in distilled water. An equal amount of solution of the catalyst was added and they were vigorously mixed together before being dried at room temperature to allow the water to evaporate. The catalyst was then heated in an oven at ∼600 °C for 4 h. A similar method was used for preparing the TiO_2 catalysts impregnated with silver.

2.3. Catalyst characterisation

Nitrogen BET (Coulter SA 3100) measurements were carried out on the supports and catalysts before plasma processing (parent samples) and the Ag/γ-Al_2O_3 catalyst samples after plasma processing in the reactor, for the one- and two-stage configurations. The results are shown in Tables 1 and 5 and discussed in Section 3.5.

3. Results

3.1. Overall results

For both benzene and toluene, the destruction was monitored whilst varying the temperature with the plasma both on and off for all catalysts and supports, giving plasma-catalysis and catalysis alone results, in both one- and two-stage configurations. The major end products CO, CO_2, NO_2, NO and N_2O were also monitored, as shown in Figs. 1 and 2. No other hydrocarbons than benzene or toluene were detected by FTIR; any other minor by-products that may be present are thus at the sub-ppm level. The NOx results from this work and other plasma-catalytic systems will be discussed in detail in future work. The results for the catalytic and plasma-catalytic destruction of toluene and benzene for temperatures between 19 and 613 °C, in both a one- and two-stage configuration, are presented in Tables 2 and 3, and Figs. 1–10. The total carbon atom balances are ∼76% for the destruction of toluene and ∼50% for benzene with higher carbon balance being achieved at the higher temperatures. Errors in the determination of concentrations are typically less than 1% and so are not specifically indicated throughout this work.

The IR spectrum of the thermal-catalytic destruction of benzene as a function of temperature using a Ag/γ-alumina catalyst is shown in Fig. 1. Thermal destruction of benzene is seen through the production of the end products CO_2 (at ∼2400 cm^{-1}) and CO (at ∼2115 cm^{-1}). CO_2 peaks start to form at ∼200 °C; this is in agreement with Kim et al. [3,13] who find that thermal destruction of benzene begins at ∼200 °C. The intensity of these CO_2 peaks increases as the temperature rises, indicating that more benzene is being converted into CO_2. Correspondingly, the peaks of benzene themselves decrease as the temperature is increased; this can be seen in Fig. 1 by the reduction of the intensity of the benzene peaks at ∼3109, 3047, 1483 and 1038 cm^{-1}. By 600 °C these peaks are very small, indicating high levels of destruction of benzene, as shown in Table 2.

A similar but slightly more complicated IR spectrum is shown in Fig. 2 for the plasma-catalytic destruction of benzene on the same catalyst, as a function of temperature. The major
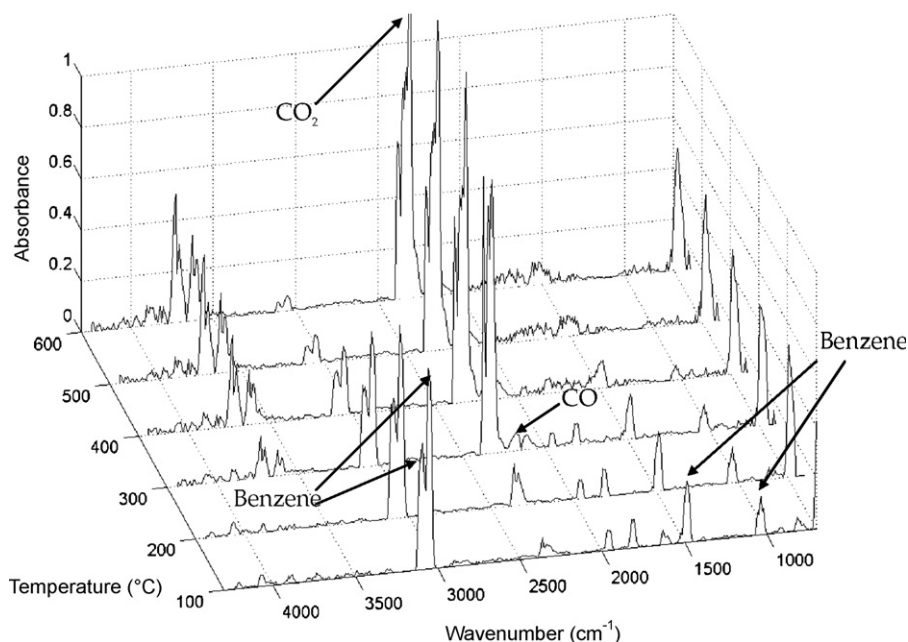

Fig. 1. IR spectra showing the thermal-catalytic destruction of benzene with Ag/γ-Al_2O_3, as a function of temperature in a two-stage configuration.
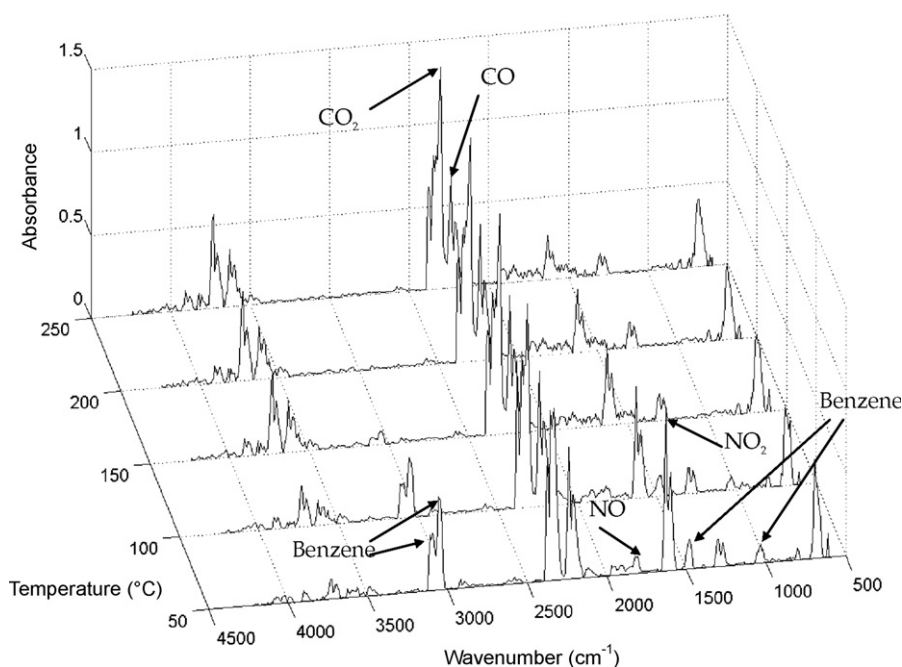
Fig. 2. IR spectra showing the plasma-catalytic destruction of benzene with $Ag/\gamma-Al_2O_3$, as a function of temperature in a two-stage configuration.

difference between the two spectra in Figs. 1 and 2 is the appearance of NO and NO_2 peaks. NO and NO_2 are both by-products of plasma destruction in air streams but are not seen during the thermal-catalytic destruction of benzene (Fig. 1) over the temperature range of these experiments. The amounts of both NO_2 and NO increase with increasing temperature, although the amount of NO is significantly lower than that of NO_2. Another difference between the two spectra is that higher levels of destruction of benzene are seen at lower temperatures for plasma-catalysis. This is illustrated in Fig. 2 by a large reduction in the intensity of the benzene peaks, especially at ~ 3109 and $\sim 3047 \, cm^{-1}$, as the temperature is increased.

3.2. Comparison of the destruction efficiencies of catalysis and plasma-catalysis

The comparison of the catalytic and plasma-catalytic destruction of toluene, in a one-stage configuration using γ-Al_2O_3 and Ag/γ-Al_2O_3 catalysts, is shown in Fig. 3a. Both the catalysis and plasma-catalysis methods increase the destruction of toluene as the temperature is increased. For both catalysts, the catalytic decomposition is much lower than the plasma-catalytic decomposition at all temperatures. At $\sim 120 \, ^{\circ}C$, the plasma-catalytic destruction of toluene, using γ-Al_2O_3, is 66%

Table 2

One-stage results for the catalytic and plasma-catalytic destruction (%) of toluene (a) and benzene (b) in air at a range of temperatures where C = catalysis alone and P = plasma-catalysis

Temperature ($^{\circ}C$)	TiO_2		Ag/TiO_2		Al_2O_3		Ag/Al_2O_3	
	C	P	C	P	C	P	C	P
(a) Toluene								
19			2	47	5	65	8	65
139	4	14	2	48	6	72	7	66
257	13	19	8	68	21	78	21	85
385	67	81	61	90	79	99	82	100
480	77	91	86		98	100	98	100
(b) Benzene								
19	17	66	7	60	24	52	4	49
143	21	69	0	59	0	54	0	48
264	42	72	5	64	7	62	0	61
387	64	79	41	77	15	76	51	94
499	61		56		56		84	

Table 3

Two-stage results for the catalytic and plasma-catalytic destruction (%) of toluene (a) and benzene (b) in air at a range of temperatures where C = catalysis alone and P = plasma-catalysis

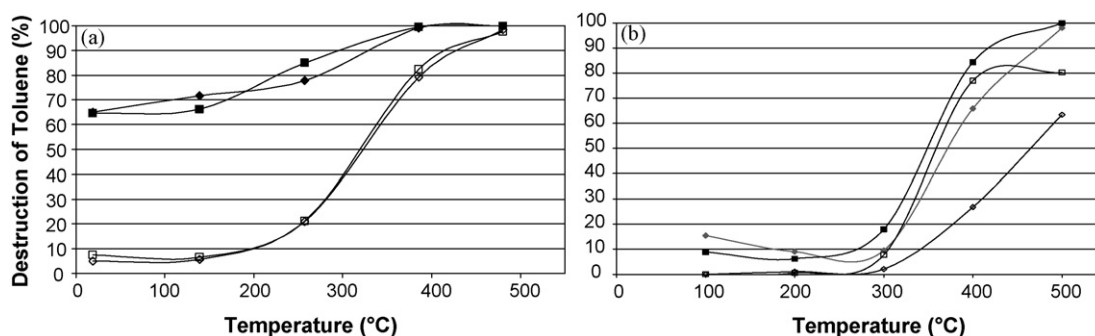| Temperature ($^{\circ}C$)	TiO_2		Ag/TiO_2		Al_2O_3		Ag/Al_2O_3	
	C	P	C	P	C	P	C	P
(a) Toluene								
19	9	47	6	39	5	24	10	28
156	10	49	7	39	6	29	14	36
247	26	52	26	48	10	31	27	48
339	50	55	61	73	35	67	54	85
430	56	66	73	82	64	96	89	100
522	77	83	89	93	86	100	98	100
613	93	95	94	96	97	100	100	100
(b) Benzene								
19	8	34	18	46	6	28	16	39
156	9	36	23	45	14	39	12	37
247	27	37	41	49	22	41	17	40
339	33	40	45	52	43	63	44	64
430	40	49	60	66	66	96	70	92
522	65	72	85	88	91	100	89	98
613	81	85	92	95	98	100	95	99

Fig. 3. Comparison of catalysis alone (open symbols) and plasma-catalysis (filled symbols) methods for the destruction of toluene at varying temperatures, using (◆, ◇) γ-Al$_2$O$_3$ support and (■, □) Ag/γ-Al$_2$O$_3$ catalyst, in a one-stage configuration: (a) this work and (b) previous results adapted from Ref. [7].

higher than the corresponding catalytic destruction; the difference between the two decreases to 18% at ~380 °C. At the maximum temperature of ~500 °C, almost total destruction of toluene is achieved by both techniques. There is little difference in the behaviour of the two catalysts over the temperature range. In the two-stage configuration, as detailed in Table 2, both the catalytic and plasma-catalytic destruction of toluene increases with increasing temperature. The plasma-

catalytic destruction is greater than the catalytic method although this difference is not as great as that seen in the one-stage configuration, as shown in Fig. 3a. At all temperatures, Ag/γ-Al$_2$O$_3$ destroys toluene more effectively than γ-Al$_2$O$_3$ in the two-stage configuration.

Fig. 3b shows a direct comparison to Fig. 3a and is adapted from our previous work [6] which used a different experimental setup. There are also some experimental differences including flow rate, initial concentration of pollutant and amount of catalyst used, which make it difficult to make a direct
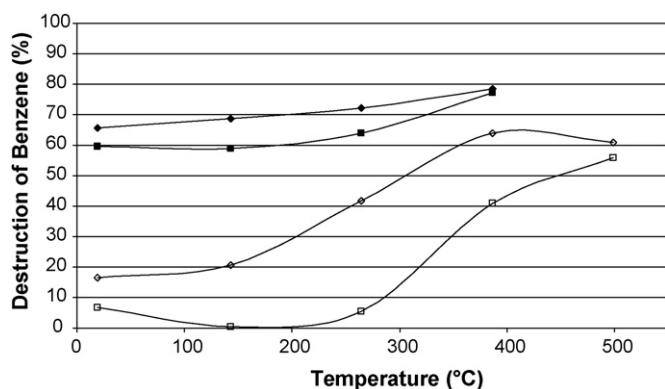

Fig. 4. Comparison of catalysis alone (open symbols) and plasma-catalysis (filled symbols) methods for the destruction of benzene at varying temperatures, using (◆, ◇) TiO$_2$ and (■, □) Ag/TiO$_2$ catalysts and supports, in a one-stage configuration.
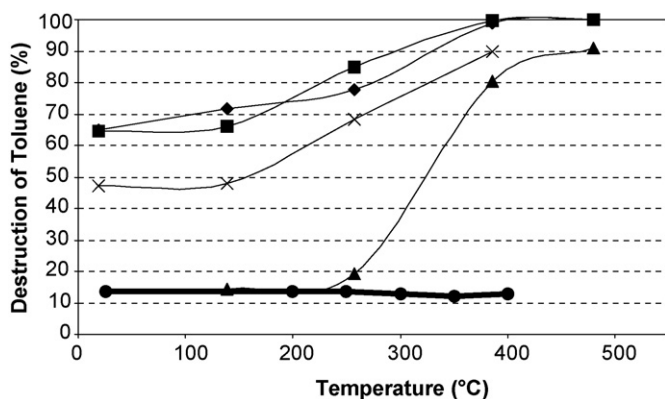

Fig. 6. Comparison of catalyst performance for the plasma-catalytic destruction of benzene at varying temperatures, using (◆) γ-Al$_2$O$_3$, (■) Ag/γ-Al$_2$O$_3$, (▲) TiO$_2$ and (×) Ag/TiO$_2$ catalysts and supports, in a one-stage configuration.

Fig. 5. Comparison of catalyst performance for the plasma-catalytic destruction of toluene at varying temperatures, using (◆) γ-Al$_2$O$_3$, (■) Ag/γ-Al$_2$O$_3$, (▲) TiO$_2$ and (×) Ag/TiO$_2$ catalysts and supports, in a one-stage configuration. The thick black line shows plasma alone results, with no catalyst.
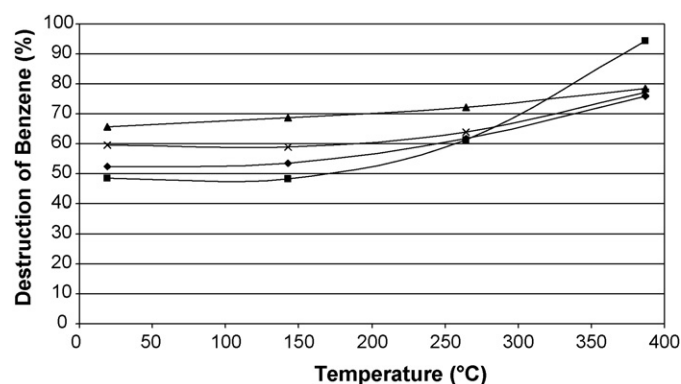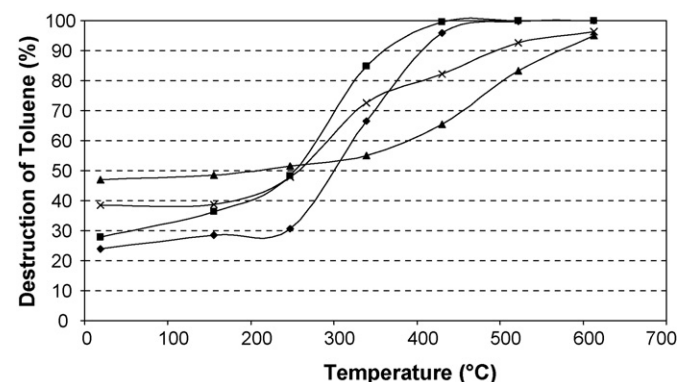

Fig. 7. Comparison of catalyst performance for the plasma-catalytic destruction of toluene at varying temperatures, using (◆) γ-Al$_2$O$_3$, (■) Ag/γ-Al$_2$O$_3$, (▲) TiO$_2$ and (×) Ag/TiO$_2$ catalysts and supports, in a two-stage configuration.
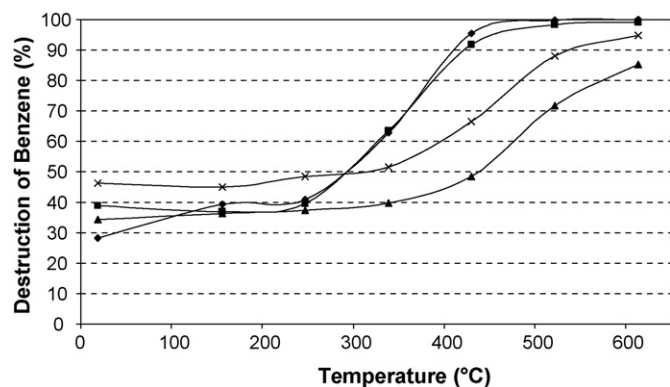
Fig. 8. Comparison of catalyst performance for the plasma-catalytic destruction of benzene at varying temperatures, using (◆) γ-Al$_2$O$_3$, (■) Ag/γ-Al$_2$O$_3$, (▲) TiO$_2$ and (×) Ag/TiO$_2$ catalysts and supports, in a two-stage configuration.
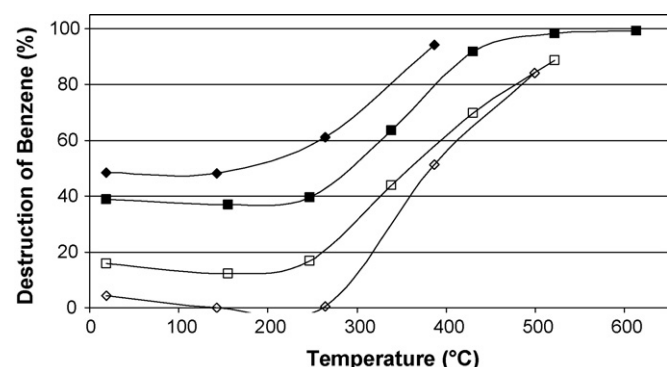

Fig. 9. Comparison of catalysis (open symbols) and plasma-catalysis (filled symbols) at varying temperatures, for (◆, ◇) one-stage and (■, □) two-stage configurations with benzene and Ag/γ-Al$_2$O$_3$ catalyst.

comparison, however, the differences in flow rate and amount of catalyst allow us to make direct comparisons of the gas hourly space velocity (GHSV) for both systems. GHSV is often a key factor in determining the performance of thermal catalyst processes [14]. In the present work, the GHSV for the one-stage configuration is 8571 h^{-1} compared to 60,000 h^{-1} in our previous work with a different experimental setup [6]; ~7 times greater. This difference is because our previous work used a

Fig. 10. Comparison of catalysis (open symbols) and plasma-catalysis (filled symbols) at varying temperatures, for (◆, ◇) one-stage and (■, □) two-stage configurations with toluene and Ag/γ-Al$_2$O$_3$ catalyst.

lower volume of catalyst (2 cm^3) in comparison to this work (7 cm^3) and also a higher flow rate (2 compared to 1 L min^{-1}). The lower GHSV value seen in this work implies more interaction of the gas with the catalyst and also a greater opportunity for plasma activation. This may explain the different shapes of the curves in Fig. 3a and b. In this study (Fig. 3a), it appears that there is a large difference between the temperature dependence of the plasma catalytic destruction and catalytic destruction for toluene which is very different to Fig. 3b where the catalysis and plasma-catalysis processes show a similar temperature dependence; whereas in the current work (Fig. 3a) there is only a very small dependence on temperature for plasma-catalysis. The larger volume of catalyst used in the present study may also means that electron-induced surface processes become more important. Such processes show only a small temperature dependence, as will be discussed below. In their study of plasma-catalytic decomposition of benzene, Kim et al. [15] found that varying the GHSV from 11,000 to 55,000 h^{-1} did not affect benzene conversion, as long as the deposited energy was kept constant. In this work and the previous study, the deposited energy value is kept constant at 60 J L^{-1}, which allows further direct comparison. The experiment yields energy efficiencies of 55 g kW h^{-1} at 256 °C in this work and 4 g kW h^{-1} at 300 °C in the previous work and also 52 g kWh^{-1} at 385 °C in this work and 17 g kW h^{-1} at 400 °C in the previous work indicating increased energy efficiency in the present work.

A comparison of the TiO$_2$ support and Ag/TiO$_2$ catalysts for the one-stage plasma-catalytic destruction of benzene is given in Fig. 4. This shows that plasma-catalysis is also more effective than catalysis alone with TiO$_2$-based catalysts. The TiO$_2$ support is more effective at destroying benzene than the Ag-impregnated TiO$_2$ catalyst, which means there is no advantage in using the Ag-impregnated catalyst over the Ag support for the destruction of benzene in the one-stage configuration. In the two-stage configuration, as shown in Table 2, there is less separation between the catalysis and plasma-catalysis results, although for both catalysts as the temperature is increased the plasma-catalytic destruction is always greater than for the catalyst alone.

3.3. Catalyst performance

A comparison of the performance of γ-Al$_2$O$_3$, Ag/γ-Al$_2$O$_3$, TiO$_2$ and Ag/TiO$_2$ catalysts for the plasma-catalytic destruction of toluene in the one-stage configuration is shown in Fig. 5, together with the plasma alone results where there is no catalyst present. This illustrates the advantage of using plasma combined with catalyst rather than just plasma alone, as regardless of the temperature when no catalyst is used the destruction of toluene remains constant at ~13%. Similar behaviour was noted in our previous study of plasma catalysis for the destruction of DCM [7]. There appears to be no advantage in adding Ag to the γ-Al$_2$O$_3$ support for the destruction of toluene in a one-stage configuration, as Figs. 3 and 5 both show little difference between the destruction of toluene on the γ-Al$_2$O$_3$ support alone and the Ag-impregnated
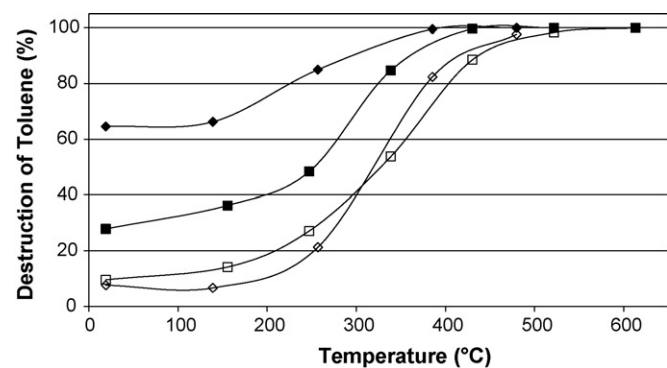
γ-Al$_2$O$_3$ catalyst. On the other hand, there is a large difference in the destruction of toluene between the TiO$_2$ support and the Ag-impregnated TiO$_2$ catalyst. At 257 °C, there is 68% toluene destruction using the Ag/TiO$_2$ catalyst, in comparison to only 19% for the TiO$_2$ support.

There is little difference between the catalysts and supports at all temperatures for the plasma-catalytic destruction of benzene in a one-stage configuration, as shown in Fig. 6. Except for Ag/γ-Al$_2$O$_3$, the plasma-catalytic destruction shows a relatively weak temperature dependence. At 150 °C, the γ-Al$_2$O$_3$ support destroys 54% benzene, in comparison to 48% with the Ag/γ-Al$_2$O$_3$ catalyst. However, by 400 °C, the Ag/γ-Al$_2$O$_3$ catalyst destroys 18% more benzene than the γ-Al$_2$O$_3$ support. The TiO$_2$ support destroys 69% benzene at 150 °C in comparison to 59% for the Ag/TiO$_2$ catalyst but at 400 °C both the TiO$_2$ support and Ag/TiO$_2$ catalyst show similar destructions of benzene (79% and 77%, respectively).

In the one-stage configuration, there would appear to be no advantage in using a Ag-impregnated γ-Al$_2$O$_3$ catalyst over the simple γ-Al$_2$O$_3$ support for destroying benzene and toluene. The same is true for TiO$_2$ at higher temperatures but at lower temperatures (up to 400 °C) use of the Ag/TiO$_2$ catalyst within the plasma destroys toluene more effectively than does the TiO$_2$ support.

A comparison of the performance of γ-Al$_2$O$_3$, Ag/γ-Al$_2$O$_3$, TiO$_2$ and Ag/TiO$_2$ catalysts for the plasma-catalytic destruction of toluene in the two-stage configuration is shown in Fig. 7. These curves show a more distinct variation with temperature than was seen for benzene. In the two-stage configuration, up to 250 °C, the TiO$_2$ support is more effective at destroying toluene than the Ag/TiO$_2$ catalyst, in contrast to the Ag/γ-Al$_2$O$_3$ which is more effective than the γ-Al$_2$O$_3$ support. Above this temperature, there is a change in the pattern of destruction of toluene using the different supports and catalysts. The TiO$_2$ support becomes less effective at destroying toluene than the Ag/TiO$_2$ catalyst. By 430 °C, 100% destruction of toluene is seen with the Ag/TiO$_2$ catalyst in comparison to 66% with the TiO$_2$ support. A similar pattern is seen with the γ-Al$_2$O$_3$ support and Ag/γ-Al$_2$O$_3$ catalyst, with the Ag/γ-Al$_2$O$_3$ catalyst destroying 18% more toluene than the γ-Al$_2$O$_3$ support at 339 °C.

In the two-stage configuration, the Ag/TiO$_2$ catalyst destroys benzene more effectively than the TiO$_2$ support, by ~10%, at all temperatures as shown in Fig. 8. A less pronounced difference is seen between the γ-Al$_2$O$_3$ support and the Ag/γ-Al$_2$O$_3$ catalyst which both destroy benzene by a similar amount over the temperature range. This means there is little advantage in using the Ag/γ-Al$_2$O$_3$ catalyst over the γ-Al$_2$O$_3$ support for destroying benzene in the two-stage configuration.

3.4. Comparison of one- and two-stage reactor configurations

The effectiveness of catalysis and plasma-catalysis in both a one- and two-stage configuration is compared. A comparison of the two configurations for the destruction of benzene, using Ag/γ-Al$_2$O$_3$ as the catalyst, is given in Fig. 9 and toluene in Fig. 10.

Table 4
BET results for Ag/γ-Al$_2$O$_3$ catalyst samples after ~20 h of plasma-catalytic processing

Pollutant gas	Reactor configuration	Surface area (m^2 g^{-1})
Toluene	One-stage	189.99
Benzene	One-stage	210.1
Toluene	Two-stage	162.75
Benzene	Two-stage	180.06

This shows that in the one- and two-stage configuration plasma activation destroys benzene and toluene more effectively than thermally activated catalytic decomposition. For catalysis alone with benzene, the two-stage configuration destroys benzene more effectively than the one-stage. There is little difference for toluene between the one- and two-stage configurations in the catalytic destruction methods of destruction in the two-stage configuration.

3.5. Catalyst characterisation

The BET measurements for the supports and catalysts before use (parent samples) have been given in Table 1. The surface area of the parent γ-Al$_2$O$_3$ support is much greater than that of TiO$_2$. Silver doping of the parent support causes a reduction in the surface area of both catalysts, as large as 90% for Ag/TiO$_2$ but only 20% for Ag/γ-Al$_2$O$_3$.

Table 4 gives the final surface areas for the Ag/γ-Al$_2$O$_3$ catalyst after ~20 h of use in both one- and two-stage configurations for the plasma catalytic destruction of benzene and toluene. In the one-stage configuration the surface area of Ag/γ-Al$_2$O$_3$ is unchanged by the processing of toluene but it increases by 10% for benzene. The two-stage configuration gives small reductions in the surface area of the Ag/γ-Al$_2$O$_3$ than one-stage processing; a 15% reduction is seen in toluene and 6% in benzene. However, these do not represent significant degradation of the catalyst under any of the experimental conditions.

4. Discussion

In this discussion we specifically draw a comparison between conventional thermal catalysis and plasma-catalysis, the different catalysts and supports, alongside their effect on the destruction of the pollutant gases of toluene, benzene and the differences in results for the one- and two-stage reactor configurations.

4.1. Mechanism of destruction

The reaction mechanisms for toluene and benzene decomposition in a non-thermal plasma have been discussed previously [6,8]. It was noted that toluene is destroyed more easily than benzene is because benzene is a very stable molecule and is harder to oxidise either in the gas-phase or on a surface than toluene. In toluene, the methyl group will readily dissociate from the aromatic ring allowing easier access to the ring and hence greater destruction in the oxidation process.

4.2. Comparison of catalysis and plasma-catalysis

We find that in the majority of cases the destruction of benzene and toluene by plasma-catalysis in a one-stage configuration is only weakly dependant on temperature in contrast to thermal catalysis which exhibits a sharply defined temperature threshold followed by a rapid rise in removal of the pollutant. However, there are also cases where plasma-catalysis shows a temperature profile similar to that for thermal catalysis such as the plasma-catalytic destruction of toluene using TiO_2 in a one-stage configuration (Fig. 5) and most of the results obtained using the two-stage arrangement (Figs. 7 and 8). It should be noted however, that plasma-activated catalysis is always more efficient than thermal catalysis in both configurations at all temperatures. The existence of these two different generic temperature profiles for plasma-activated catalysis has been taken to indicate that there may be two contributing mechanisms for plasma-activated catalysis; the first being temperature independent whereas the second is temperature dependent with a threshold at a certain temperature in a similar manner to thermal catalysis but generally shifted to lower temperatures [6].

It is known that the rates of electron impact and electron attachment processes are not strongly dependent on temperature, whereas radical-based chemistry generally has a large temperature dependence [16] and there may be large barriers for surface adsorption and desorption. It is possible that the key rate-determining step in the mechanism of the plasma-catalytic destruction of benzene involves electron impact processes whereas the catalytic destruction of benzene could be dominated by the rates of radical-based chemistry in the gas-phase or on the surface. There is also the possibility that electron-surface initiated processes are taking place in the plasma in the one-stage configuration that may be responsible for the difference in the temperature dependences which of course are not present in conventional catalytic decomposition. Kim et al. [17] have suggested that electron-induced processes will not show significant temperature dependence as the electrons in the plasma already have sufficient energy without the need for extra heating and that catalyst activation due to electrons will show no temperature dependence.

We can compare our thermal catalysis results with those of Li and Chen [18] who catalytically incinerated benzene over TiO_2 and mixed TiO_2 catalysts. At 390 °C, they obtained 50% conversion of benzene using TiO_2 alone, compared to our results which show 50% conversion at ~300 °C. We find that the maximum destruction of benzene using the TiO_2 catalyst, with no plasma, is 64% at 387 °C. Li and Chen [18] found that 650 °C was required to destroy 99% of the benzene.

4.3. Catalyst performance under plasma activation

The use of a catalyst in conjunction with plasma gives much better destruction of pollutants; when the plasma is operated on its own 13% destruction of toluene is seen regardless of the temperature (Fig. 5). In contrast, when a catalyst is used the destruction of toluene increases with temperature. In the one-stage configuration, use of the γ-Al_2O_3 support destroys toluene better than does the TiO_2 support at all temperatures. With benzene, there is generally little difference between the performances of the catalysts at different temperatures. At low temperatures, TiO_2 destroys toluene better than Ag/TiO_2, although at temperatures greater than 300 °C this trend is reversed with Ag/TiO_2 destroying toluene more effectively. This same pattern of temperature dependence is seen with TiO_2 destroying toluene more effectively than γ-Al_2O_3 at lower temperatures with the reverse again at higher temperatures. At high temperatures (>573 K), γ-Al_2O_3-based catalysts show most promise due their durability at high temperatures and high thermal activity, in contrast at lower temperatures (423–543 K) where better success is seen using catalysts based on zeolite Y supports in plasma operation [19].

With benzene again there is little difference in the performance of the catalysts, although Ag/TiO_2 destroys benzene most effectively and is a better catalyst than TiO_2. Yet again a pattern of temperature dependence is seen with both the γ-Al_2O_3-based catalysts destroying benzene more effectively than the TiO_2-based catalysts at high temperatures. Yamamoto et al. [20] find that the decomposition efficiency of a packed-bed plasma reactor using Ni-supported $BaTiO_3$ pellets is higher than using uncoated $BaTiO_3$ pellets. This led the group to carry out further work studying the effects of transition metals supported on γ-Al_2O_3 [21,22] finding that using Ag, Co, Cu and Ni-supported γ-Al_2O_3 catalysts increased benzene decomposition by ~10–20%. It is well known that the addition of transition metals to γ-Al_2O_3 enhances catalytic activity [19,23]. The group of Ogata et al. have carried out much work looking at the non-thermal plasma destruction of benzene [24,25] combined with the use of various catalysts [26] including extensive studies using γ-Al_2O_3 [21,22,27]. They find that oxidative decomposition of benzene is enhanced using γ-Al_2O_3 pellets, and that the use of the γ-Al_2O_3 catalyst causes the energy efficiency to be improved and by-product formation to be suppressed [26,27].

4.4. Comparison of one- and two-stage reactor configurations

A direct comparison of the one- and two-stage systems was made by modifying the setups so that both systems contained the same amount of catalyst. It was generally found that the plasma decomposition of toluene in a two-stage configuration is greater using a smaller amount of catalyst. The same pattern is seen in the catalytic decomposition of toluene in the two-stage configuration below 300 °C, with the smaller amount of catalyst showing higher decomposition, although at higher temperatures the amount of catalyst has no effect on the decomposition. These observations will be taken into consideration when directly comparing the one- and two-stage systems.

In the one-stage configuration, plasma catalysis is found to be more effective at destroying both benzene and toluene than catalysis alone over the entire temperature range for Ag/γ-Al_2O_3. The same is not true in the two-stage configuration, with

thermal catalysis more effectively destroying benzene than plasma-catalysis. With toluene there is little difference between the two methods in the two-stage configuration. This is also seen by Roland et al. [28], who find that the one-stage configuration shows higher destruction efficiency than the two-stage configuration.

In the one-stage process, with the catalyst inside the discharge, the process of plasma-catalysis promotes electron- and photon-induced processes, surface-discharges creating surface sites that promote oxidation. The discharge also produces short-lived radicals and intermediates such as ozone which may participate in decomposition reactions both in the gas-phase and on the catalyst surface [29,30].

Catalytically, there is little difference in the destruction of toluene using either the one or two-stage configuration, although for benzene the two-stage configuration is more effective than the one-stage configuration. Almost 50% destruction is seen for benzene and 65% for toluene at room temperature for plasma-catalysis in the one-stage configuration, compared with 39% and 29% for the two-stage configuration. This indicates that it is plasma generated species in the one-stage configuration that are responsible for destroying the pollutants and these are absent in catalytic decomposition at room temperature. Kim et al. [17] note that plasma-induced surface reactions may play an important role in the destruction of benzene in the one-stage configuration as well as gaseous plasma-induced species. When the catalysis results from Tables 2 and 3 are compared, in most cases a considerable difference in the conversion of VOCs is seen in the one- and two-stage results; generally much higher levels of conversion are seen in the two-stage than the one-stage. In the case of catalysis alone, the plasma is not being utilised so the destruction is not enhanced in the one-stage system by the excited species produced by the plasma, which directly react with the catalyst. Instead the combination of barium titanate beads, which are used to give the plasma discharge, with the catalyst in the one-stage system may be preventing the catalyst working as effectively than when placed downstream of the system in the two-stage system. It is not expected that barium titanate beads will have any adsorbent properties.

This difference between the two configurations could be due to plasma activation of the catalyst, as radicals, electrons and photons created by the plasma can directly interact with the catalyst and molecules adsorbed on its surface in the one-stage configuration, thus enhancing destruction. This synergistic effect of the plasma-catalysis system has been noted before by Ogata et al. [27], who see an increase of 10–20% in destruction in the one-stage plasma reactor alone. Ogata et al. also find that benzene oxidation takes place in the gas phase in the one-stage configuration and they say that the slower response they see in the two-stage configuration arises from desorption and adsorption of benzene onto the γ-Al$_2$O$_3$ pellet layer [21,27].

Toluene is destroyed much more effectively than benzene, independent of the temperature of the system, in both one- and two-stage configurations. This is the same as found previously [6]; even though these results were performed under slightly different experimental and reactor conditions this same trend was still seen. This difference reflects the mechanism of destruction in both the gas- and surface-phases which is more facile for toluene than for benzene.

5. Conclusions

Plasma-catalysis is more effective at destroying both benzene and toluene than conventional thermal-catalysis, and plasma alone. In the one-stage configuration, the use of γ-Al$_2$O$_3$ destroys toluene better than TiO$_2$. With benzene, there is generally little difference in the destruction efficiencies for the catalysts with temperature. In the two-stage configuration, TiO$_2$ works most effectively at lower temperatures, whereas γ-Al$_2$O$_3$ is more effective at higher temperatures. Toluene is destroyed much more effectively than benzene, regardless of the temperature of the system and the reactor configuration. A one-stage, plasma-catalysis configuration is more effective at destroying both toluene and benzene than a two-stage configuration. Catalytically, there is little difference in the destruction of toluene with either configuration, although the two-stage configuration is more effective at thermally destroying benzene. There is no advantage to be gained in using plasma-catalysis over catalysis alone for destroying both pollutants in the two-stage configuration.

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